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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY

VOLUME 8: VINYL CHLORIDE MANUFACTURE BY THE BALANCED PROCESS

AIR PRODUCTS AND CHEMICALS, INCORPORATED

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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY VOLUME 8: VINYL CHLORIDE MANUFACTURE BY THE BALANCED PROCESS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c, and d).

This volume covers the manufacture of vinyl chloride by the balanced process. Included is a process and industry description, an engineering description of available emission control systems and the cost of these systems.

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In-Depth Study

of

VINYL CHLORIDE MONOMER PRODUCTION

Contract No. 68-02-0255

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Prepared By

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Houdry Division

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume), high density polyethylene, polyvinyl chloride and vinyl chloride monomer.

ACKNOWLEDGEMENTS

The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of vinyl chloride monomer. This was given at a particularly difficult time as all the companies were in the midst of an all out effort to reduce all vinyl chloride monomer emissions to a minimum. Without their information this report could not have been written. We, therefore, list the participating companies to acknowledge their cooperation and assistance.

Allied Chemical Corporation
American Chemical Corporation*
Continental Oil Company
Monochem, Inc.
PPG Industries, Inc.
Shell Chemical Company
Tenneco Chemical, Inc.

*Subsidiary of Stauffer Chemical Company

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I. Introduction

The production of vinyl chloride monomer (VCM) has become a big volume business. Some of the older existing plants are in the 150 to 200 million pounds per year capacity range. It is believed that virtually all new plants will be designed to produce in excess of 500 million pounds of VCM per year.[1] This is because the economics of production definitely favor large volume raw material supply and large equipment. Almost all the VCM produced goes into the manufacture of polyvinyl chloride (PVC). A very small amount is used as an intermediate to manufacture methyl chloroform ($CH_3{\cdot}CCl_3$), a specialty solvent. A small quantity was previously used in special aerosol sprays (insecticides, fungicides, etc.) but this use has recently been banned in the United States. Therefore the growth of VCM is exactly tied to the growth of PVC. In 1973 total U.S. production of VCM exceeded 4.7 billion pounds.[2]

Over ninety percent of the vinyl chloride monomer produced in the United States is obtained by cracking dichloroethane. An older process using acetylene and hydrogen chloride feed has been virtually completely replaced by the dichloroethane route because of the high cost of acetylene. The capacity of acetylene type plants is about 10-12% but actual production from them is much less.

In most cases, overall vapor emissions from the cracking operation are small in quantity. The vapor emissions do include a small amount of VCM. The problems of VCM air emissions in these plants are similar to those encountered in PVC production. However, VCM plants have one big advantage, they employ a continuous process as opposed to the PVC batch type processes. This means that VCM emissions from these plants are considerably less per unit of production.

This report concentrates on VCM emissions, not hydrocarbon and particulate losses. It also contains information on VCM losses from ethylene dichloride (EDC) plants using the oxychlorination process. This latter information was not included in a previous in-depth study of the oxychlorination process.[4] Prior to January 1974 it was not known that VCM was carcinogenic at low concentrations (under 500 PPM). Because of this, EDC manufacturers had not attempted to analyze or report the presence of VCM in the oxychlorination vent streams.

The emission losses used in the present report are based on information obtained prior to September 1974. There has been much money and effort spent to reduce VCM emission losses from EDC and VCM manufacture since that time as well as much improvement made in the detection of low concentrations of VCM (under 10 PPM). VCM emissions have undoubtedly been substantially reduced since the summer of 1974.

II. Commercial Processes

Acetylene and hydrogen chloride are used as starting materials in the oldest commercial process. In this country, this is a minor process because economics favor ethylene as a raw hydrocarbon feedstock over acetylene. However, there are two plants still using this process.

The reaction is as follows:

$$C_2H_2 + HCl \longrightarrow CH_2 = CHCl$$

The reaction is catalyzed by mercuric chloride (10%) on an activated carbon base and is carried out at 195° to 285°F. The reactants are fed at a 1:1 mol ratio and the reaction goes to approximately 98 to 99% completion. The reaction is very exothermic and temperature must be controlled carefully. The reactor pressure is low (2.5 atm.) for safety reasons. Acetylene becomes increasingly hazardous (explosively) at elevated pressures. If acetylene could be produced nearly as cheaply as ethylene (say within a half a cent per pound), this process could compete with ethylene process as there are no major by-products to consider. However at the current differential of 5 to 10 cents per pound, the use of acetylene is too expensive to consider for any new plants and makes existing plants marginal. Figure VC-1 shows a simplified flow diagram for the acetylene process. Plants VC-7 and VC-9 are the only plants surveyed in this study that use the acetylene process.

In the principal process currently used to produce VCM, dry dichloroethane (also named ethylene dichloride) is dehydrochlorinated to vinyl chloride in a cracking furnace.

The chemical reaction is as follows:

$$CH_2ClCH_2Cl \longrightarrow CH_2 = CHCl + HCl$$

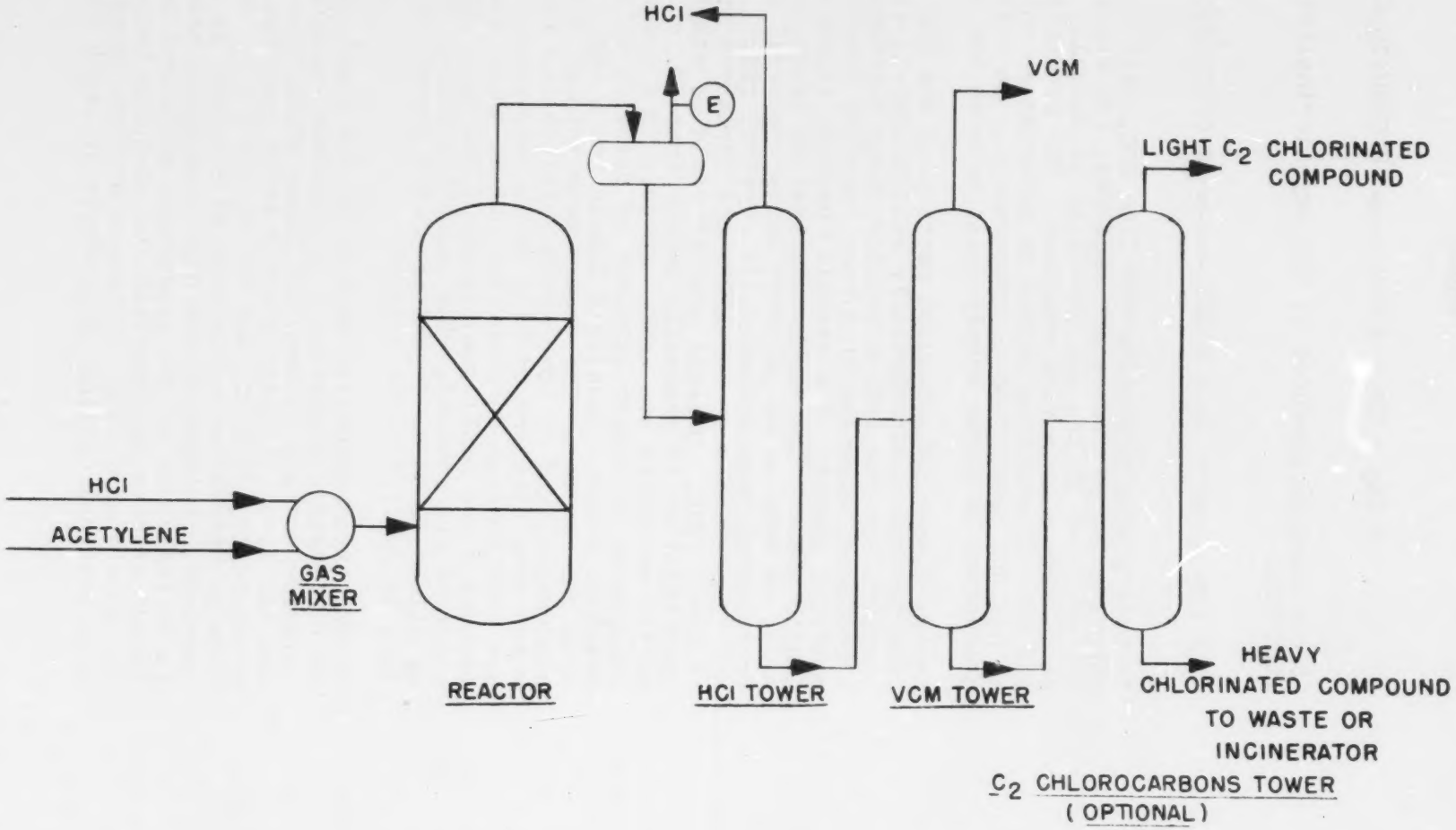
The dichloroethane for this cracking operation is normally produced by two commercial processes. One is the direct chlorination of ethylene with chlorine:

FIGURE VC-1

ACETYLENE PROCESS

FOR

VINYL CHLORIDE PRODUCTION



$$2\ CH_2 = CH_2 + 2\ Cl_2 \longrightarrow 2\ CH_2ClCH_2Cl$$

It can also be produced by the oxychlorination of ethylene with HCl:

$$2\ CH_2 = CH_2 + O_2 + 4\ HCl \longrightarrow 2\ CH_2ClCH_2Cl + 2\ H_2O$$

In most plants producing VCM from EDC, both of the above chlorination processes are employed, see Figure VC-2. All HCl produced in the EDC pyrolysis is normally used as feed to the oxychlorination reactors. The production of EDC by the two chlorination routes is balanced so that there is no net HCl production or consumption. On this basis, EDC production is about evenly split between the two processes.

In the direct chlorination section of the EDC based plant, chlorine and a substantially stoichiometric amount of ethylene are fed into a reactor under constant temperature conditions, excesses of either reactant result in raw material losses. The reaction usually takes place in the liquid phase. The exothermic heat of reaction, 52 kcal/mole, is removed by jacketed walls, internal cooling coils or external heat exchange.(3) Typical reaction conditions are temperatures of 100-120°F and pressures in the range of 10-20 PSIG. Overall process yield of ethylene dichloride from chlorine is generally better than 98 percent if high purity reactants are used. However, the presence of impurities in either ethylene or chlorine will reduce the reaction yield. Usually a liquid and a vapor stream exit from the reactor. The vapors pass through water cooled condensers, and in some cases refrigerated exchangers where some ethylene dichloride is recovered. The vapors are sent through an absorbing column where dichloride is recovered and small quantities of hydrogen chloride and chlorine are removed. The scrubbing liquid is either water or dilute caustic, depending on the amount of chlorine that is desired to be removed.

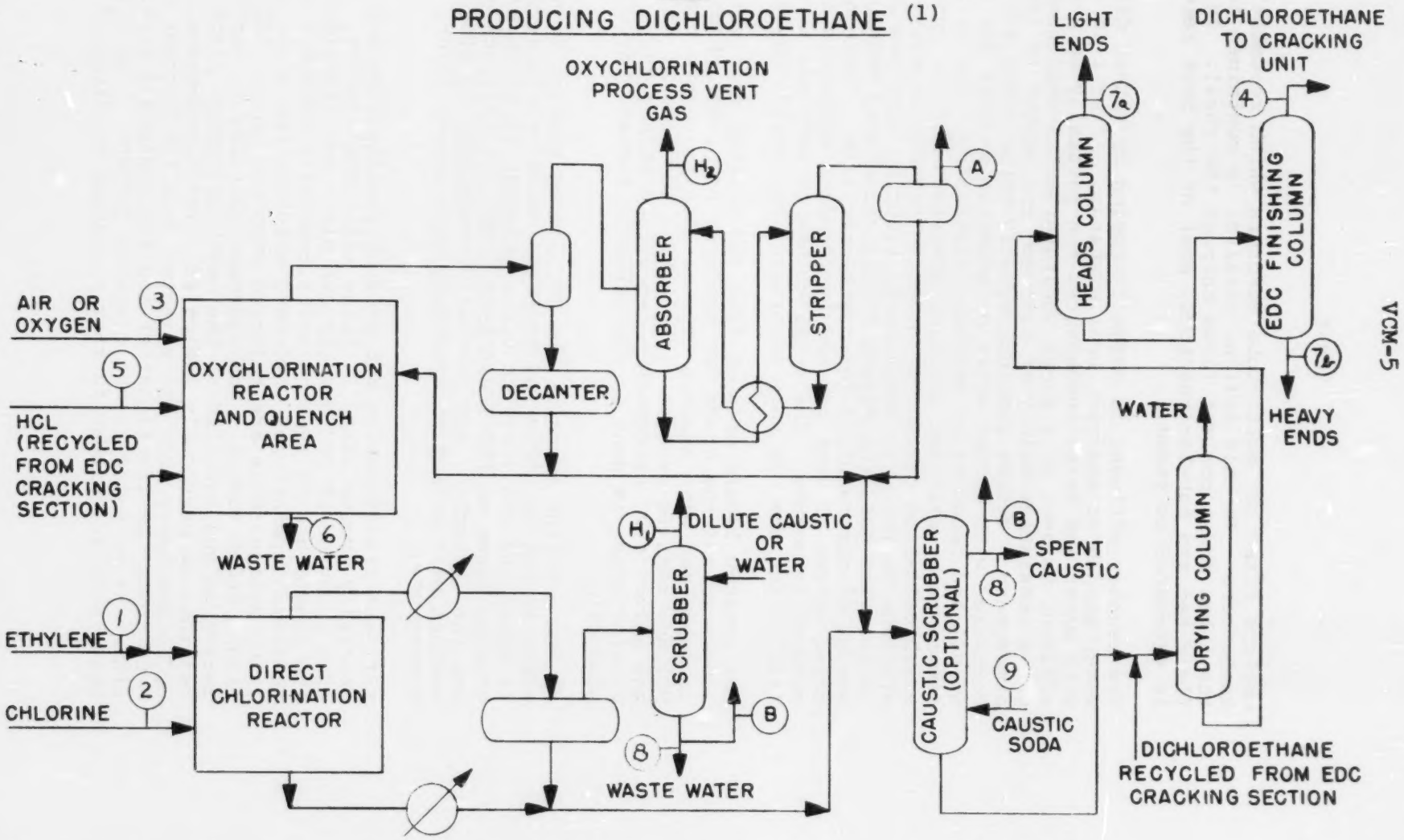
In the oxychlorination section of the plant approximately stoichiometric proportions of ethylene, anhydrous hydrogen chloride and air (except one plant which uses pure oxygen) are fed to a catalytic reactor which operates at low pressure (20-75 PSIG) and 400 to 600°F.(4) Once through flow is used since conversion of ethylene is virtually complete. Because of the high exothermic heat of reaction ($>$ 55 kcal/mole of EDC produced), efficient heat removal in the reactor is important for adequate temperature control. For this reason, some processes utilize fluid bed reactors with internal cooling coils while at least one producer

FIGURE VC-2

BALANCED CHLORINATION PROCESS

FOR

PRODUCING DICHLOROETHANE (1)



(1) Includes solvent secondary recovery of EDC from oxychlorination process vent.

employs fixed bed multi-tube reactors which resemble heat exchangers. In this design, catalyst is contained inside the tubes and a coolant flows through the shell. In both fluid bed and tubular reactors, most of the heat removed is recovered as steam.

The reactor effluent is normally cooled by either direct water quench or indirect heat exchange. After trim cooling with water and brine condensers, the partially condensed effluent is sent to a phase separator. Non-condensable gases consisting mainly of nitrogen are vented to the atmosphere. Before venting, usually these gases are contacted with either water or aromatic solvent for removal of HCl and recovery of ethylene dichloride. One process incorporates chlorine addition downstream of the main oxychlorination reactor in order to convert unreacted ethylene to EDC. In addition to reducing ethylene loss in the vent gas, the direct chlorination step reduces the amount of air required for oxychlorination. Therefore, the total volume of vent gas and hydrocarbon emissions are reduced in volume. The total volume of vent gas is even smaller for the one unit incorporating tonnage oxygen.

The organic liquid product from the reactor effluent phase separator and the crude EDC produced by direct chlorination is contacted with aqueous caustic soda to remove traces of HCl and sent to product distillation for removal of water and chlorinated hydrocarbon impurities before the dichlorethane is sent to the cracking furnace for VCM production.

In the cracking furnace, the EDC passes through furnace tubes at 900 to 950^{o}F and 50 PSIG. Dichloroethane conversion is about 50% and yield to vinyl chloride is 94 to 97 mole percent based on EDC fresh feed. The hot effluent gases are then quenched, and partially condensed, by direct contact with cold dichloroethane in a quench tower, see Figure VC-3.

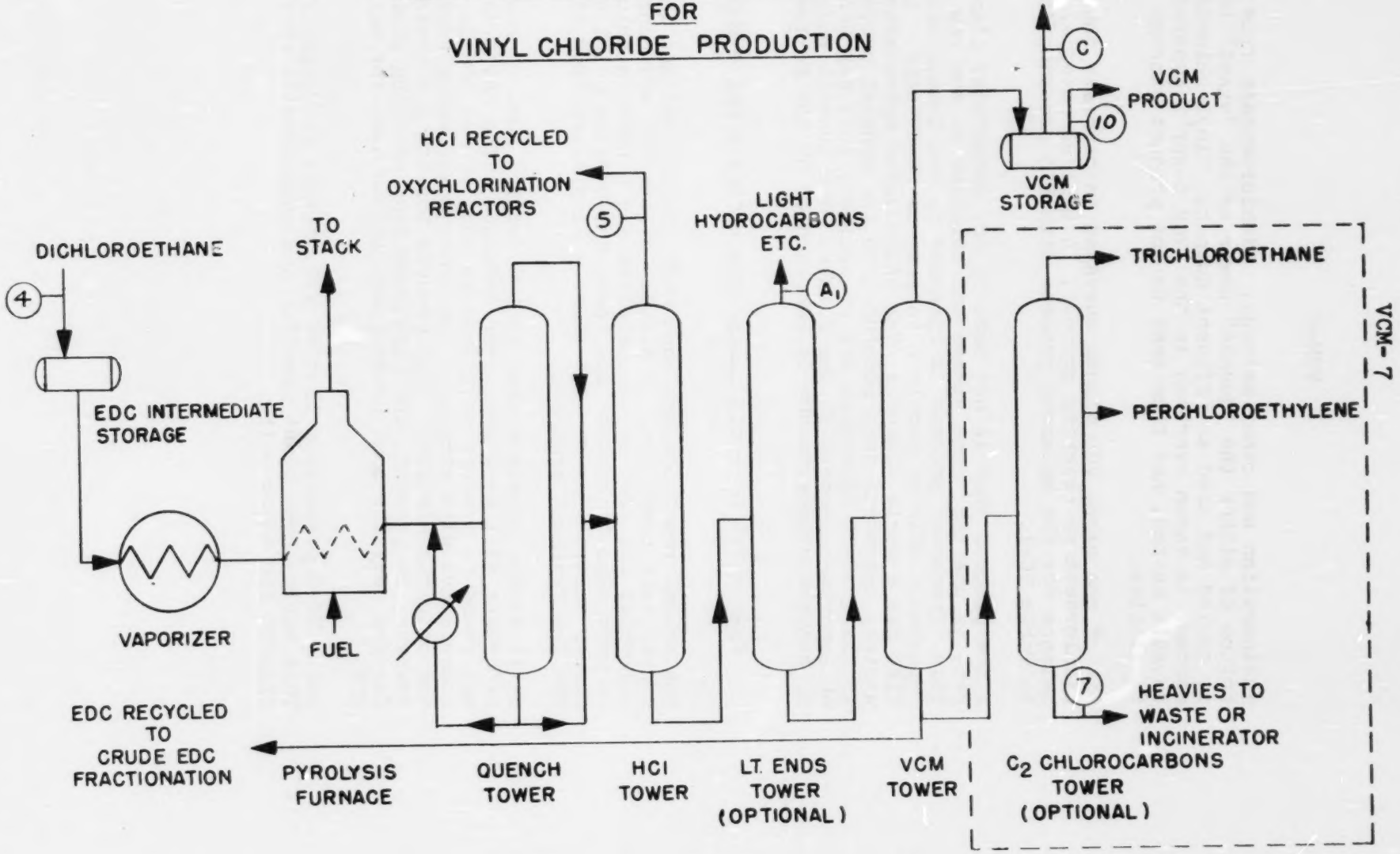
Effluent fractionation and product purification are generally accomplished in three additional towers. However, each producer of VCM has his own minor modifications in the fractionation section which typically includes the following operations. Hydrogen chloride and light chlorinated hydrocarbons are rejected overhead in the "HCl" and "Light Ends" towers. The hydrogen chloride is normally recovered and recycled to the oxychlorination plant reactors as previously indicated. Trichloroethane, and other heavy ends are rejected from the bottoms of the "VCM tower" by fractionation and the contained dichloroethane is recycled to the cracking furnace. The light and heavy ends are either further processed or disposed of by

FIGURE VC-3

DICHLOROETHANE CRACKING PROCESS

FOR

VINYL CHLORIDE PRODUCTION



incineration and other methods. Dichloroethane from the bottom of either the "quench" tower or the "vinyl" tower is cooled and used as effluent quench. Vinyl chloride monomer is taken overhead in the "VCM tower", generally caustic washed, and then sent to the product storage facilities.

Six of the eight VCM plants surveyed incorporate the dichloroethane cracking process. A typical material balance for the balanced process with EDC cracking is shown in Table VC-1.

A new process that is not used by any commercial plants as yet, is one that uses ethane and chlorine as the raw feed. This "Transcat" process is licensed by C-E Lummus and is reportedly able to handle a variety of feedstocks. It also has a waste disposal (for chlorinated hydrocarbon wastes) operation incorporated into the general process. If the overall economics are as claimed, this may become an important process in the future. The overall reaction to convert ethane to VCM is represented by the following:

$$C_2H_6 + 1/2\ O_2 + Cl_2 \longrightarrow CH_2 = CHCl + HCl + H_2O$$

The actual reactions are much more complicated and involve copper salt complexes. A mixture of cuprous and cupric chlorides are used as the catalyst and potassium chloride is used also to control and lower the melting point of the copper salts. Figure VC-4 shows a simplified flow diagram for the Transcat process.

It is always possible that in the future, more economical processes will be found. For instance, if a new process was found to produce acetylene so that it was nearly competitive with ethylene, the trend would swing back to the original acetylene type process for VCM production. However, at present, the dichloroethane cracking process is far and away the most predominate method used for making VCM.

Table VC-2 presents a list of U.S. plants producing VCM. This table shows plant location and published(5) capacity figures for these units.

TABLE VC-1

TYPICAL MATERIAL BALANCE FOR VCM PRODUCTION VIA BALANCED ETHYLENE PROCESS[5]

Stream I.D.	1	2	3	4	5	6	7a	7b	8	9	H1	H2	A & A1	10
	Raw Materials			Intermediates		By-Products			Water Streams		Vent Streams			Product
Components	C_2H_4	CL_2	Air	EDC	HCl	H_2O	Lights	Heavies	H_2O	Dilute Caustic	EDC Direct	EDC Oxy	Dist	VCM
Carbon Dioxide			0.0003								(4)	0.0116		
Carbon Monoxide											(4)	0.0032		
Nitrogen			0.5782								(4)	0.5779	0.0003	
Oxygen			0.1537								(4)	0.0214		
Chlorine		0.5871									0.0001		0.0001	
Hydrogen Chloride					0.6036									
Water			0.0171			0.1438			0.1166	0.0030		0.0413		
Caustic Soda										0.0008				
Sodium Chloride									0.0014					
Ethylene	0.4656										0.0025			
Other Hydrocarbons	0.0002												0.0001	
EDC				1.6370[1]			0.0017	0.0012			0.0016	0.0017	0.0045	
VCM							0.0008[2]				0.0001	0.0012	0.0024[2]	1.0000[3]
Light Chlorocarbons							0.0017	0.0012			0.0003	0.0025		
Heavy Chlorocarbons								0.0023						
Total, Lbs./Lb. VCM	0.4658	0.5871	0.7493	1.6370	0.6036	0.1438	0.0042	0.0047	0.1180	0.0038	0.0045	0.6609	0.0075	1.0000

Notes:

(1) The amount of EDC in this column represent the EDC necessary for a stoichiometric balance including the amount that is changed to other products (i.e., heavy chlorocarbons), but does not include any recycle EDC.

(2) VCM fugitive emissions are included in this category in order to make a material balance even though part of the actual losses occur elsewhere.

(3) Excludes storage and loading losses of VCM. The average of these losses for surveyed plants was 0.0008 lbs./lb. product.

(4) Inerts present in chlorine feed will be emitted in this vent stream.

(5) Miscellaneous intermittent emissions not noted in this material balance, such as sampling, annual vessel openings, miscellaneous fugitive emissions, etc. amount to about 0.0001 lbs/lb. product.

FIGURE VC-4

TRANSCAT PROCESS
FOR
VINYL CHLORIDE PRODUCTION

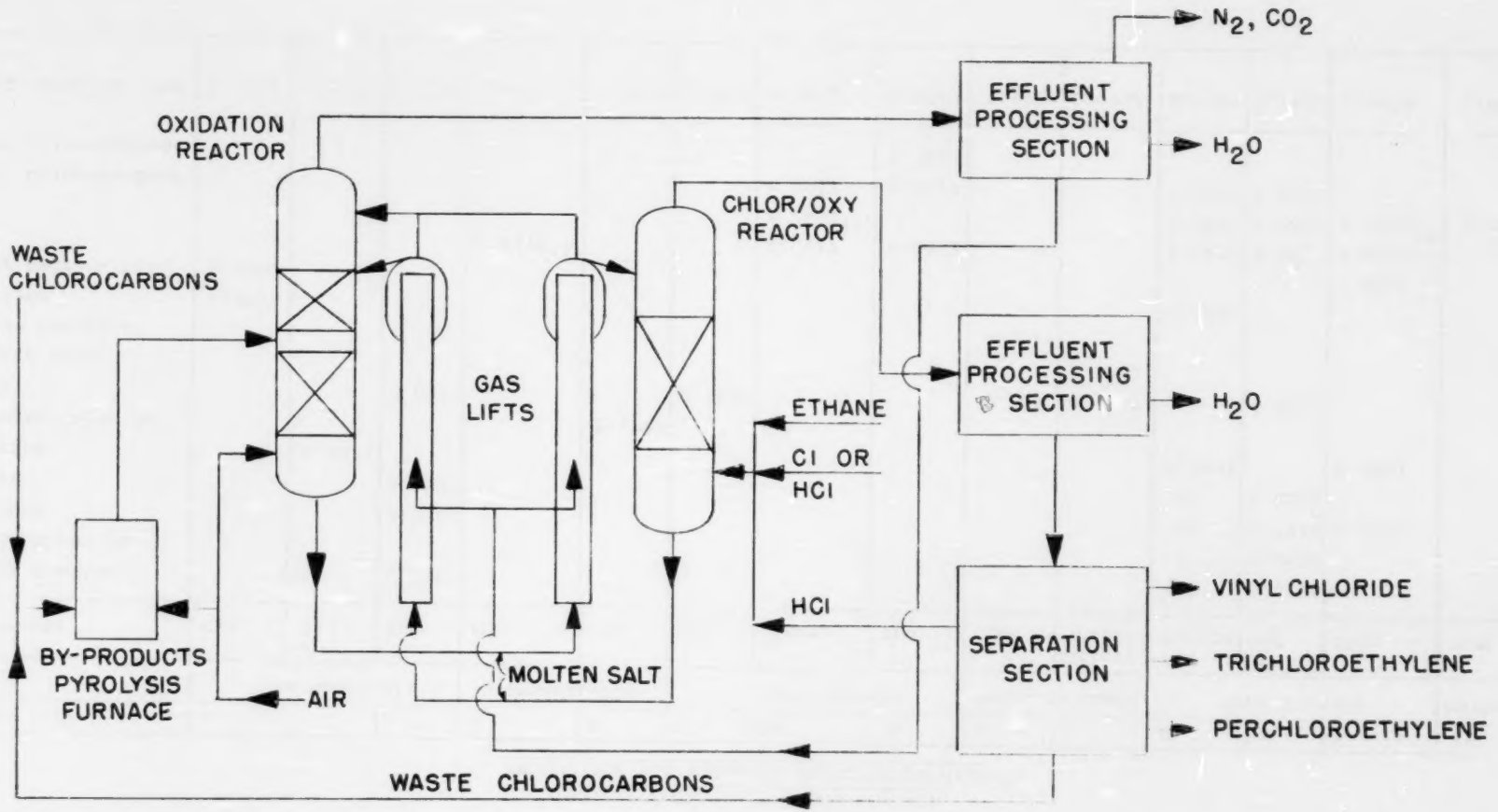


TABLE VC-2

SUMMARY OF U.S. VINYL CHLORIDE PLANTS

Company	Location	Published Capacity, MM Lbs./Yr. (5)
Allied Chemical	Baton Rouge, Louisiana	300
American Chemical	Long Beach, California	170
Conoco	Lake Charles, Louisiana	700
Dow Chemical	Freeport, Texas	180
	Plaquemine, Louisiana	340
	Oyster Creek, Texas	800
Ethyl Corporation	Baton Rouge, Louisiana	270
	Pasadena, Texas	150
B. F. Goodrich	Calvert City, Kentucky	1,000
PPG Industries	Lake Charles, Louisiana	300
	Guayanilla, Puerto Rico	575
Shell Chemical	Deer Park, Texas	840
	Norco, Louisiana	700
Monochem Inc.*	Geismar, Louisiana	300
Tenneco*	Pasadena, Texas	225
	TOTAL	6,850

* Only plants using acetylene as raw feedstock. All other plants use dichloroethane.

III. Plant Emissions

Table VC-3 shows individual plant capacity figures and VCM emission data for eight of the ten manufacturers of VCM. Emission sources from these plants are as follows:

A. Continuous Air Emissions

One company (VC-2) states that they have no continuous emission losses other than fugitive emissions and that these losses are very low based on material balance. However, they do not indicate any emissions from the oxychlorination unit where there are probably some VCM losses.

All the other companies have continuous losses which are often fed into control devices along with intermittent streams. The continuous air emissions are as follows:

1. Distillation Columns - Most of the plants have distillation columns to separate impurities from the EDC (Source Areas A & 7a) or from VCM (Source Area A_1). The inert gases from these columns (after refrigeration, scrubbing, etc.) contain some VCM. Depending on the plant, this vent is either emitted to the air or is vented to a control device.

2. Flash Drums - Several VCM plants have a flash drum to separate vinyl chloride from neutralizing water streams. The VCM vapors are generally fed to an emission control device (Source Area B).

3. Vent Reactor Vent - One acetylene plant (VC-9) has a vent reactor which is actually a small reactor designed to take the gaseous effluent from the main reactor and react as much as possible of the remaining reactants to completion (VCM). The vent from this secondary reactor is sent to the purification system where the inerts are vented to the atmosphere (Source Area E).

4. Oxychlorination Vent Gas - This stream, which generally vents from a scrubber or an absorber, consists of the gross oxychlorination reactor effluent after quenching and trim cooling for recovery of EDC. Table VC-4 shows a typical breakdown of components in this stream, which represents the primary air emission in the oxychlorination section of the plant (Source Area H_2).

   Catalyst activity, reactor operating conditions and the specific processing scheme employed have some influence on the amount of vent gas emissions from this source. For example, in one process, chlorine

TABLE VC-3

NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-1
Plant Capacity, Million Lbs./Yr.: 500
Process: Balanced EDC

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions	
				Lbs./Lb. Prod.	Tons/Yr.
7a	EDC Distillation Column (1)		VMD-1	.000175	
7a	EDC Distillation Column (2)		VMD-1	.000354	
C	Transfer and Loading Losses		VMD-1	.000048	
D	Sampling Losses	(3)	VMD-17	.000001	
	Fugitive Losses	(4)		?	
	Total			.000578	144.5

Notes:

(1) Vent from EDC column in associated direct chlorination unit.
(2) Vent from EDC column in associated oxyhydrochlorination unit.
(3) Flow sampling loops.
(4) No estimate of fugitive emission given - no material balance.

TABLE VC-3
NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-2
Plant Capacity, Million Lbs./Yr.: 300
Process: Pyrolysis of EDC

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions Lbs./Lb. Prod.	VCM Emissions Tons/Yr.
B	Released From Neutralizer Water (1)		VMD-1	.000015	
C	Dock & RR Tank Car Loading Loss (2)		VMD-2	.001214	
D	Sampling (3)		VMD-17	.000001	
F	Neutralizers and Filters (4)		VMD-1	.000002	
F&G	Dryers and Process Vessels (4)		VMD-1	.000032	
	Fugitive (5)			?	
	Total			.001264	189.6

Notes:

(1) Vent from flash pot releasing.
(2) All major VCM emission streams returned to absorber to be recycled in EDC streams. This loss will drop to approximately .000174 by mid 1975 when dock loading losses are connected to system.
(3) Sampling losses minimized by sampling loop.
(4) Intermittent emissions.
(5) No estimate or material balance given.

TABLE VC-3

NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-3
Plant Capacity, Million Lbs./Yr.: 840
Process: Balanced EDC

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions	
				Lbs./Lb. Prod.	Tons/Yr.
A	Scrubber Vent Stack - Collects From 8 Areas	None	VMD-1	.002355	
C	Loading Arms and Loading Areas			.000048	
	Flare		VMD-3 (2)	-	
D	Sampling			.000023	
	Fugitive (1)			.000052	
	Total			.002478	1040.7

Notes:

(1) Calculated by analogy from emission factors taken from "Control Techniques for Hydrocarbon and Organic Solvent Emissions From Stationary Sources", Natural Air Pollution Administration, Publisher Number AP-68, March 1970.

(2) A refrigeration device, VMD-4, is used to condense some of the vapors prior to the flare. No data are given as to conditions or type of equipment.

TABLE VC-3

NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-4
Plant Capacity, Million Lbs./Yr.: 730
Process: Balanced EDC

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions Lbs./Lb. Prod.	VCM Emissions Tons/Yr.
	Main Stack		VMD-1	.001368	
C	Loading Losses		VMD-4 (2)	.001929	
	Fugitive (1)			?	
	Total			.003297	1203.4

Notes:

(1) No estimate given or material balance made.

(2) Some type of condensing system is noted but no information is given of conditions or type of equipment.

TABLE VC-3

NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-6
Plant Capacity, Million Lbs./Yr.: 320
Process: Pyrolysis of EDC

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions Lbs./Lb. Prod.	VCM Emissions Tons/Yr.
A	Light Column Vent		VMD-1	.000040	
C	Tank Car Loading			.000486	
D	Sampling		VMD-17	.000001	
G	Cleaning, Inspections, Etc. of Vessel			.000088	
	Fugitive (1)			?	
	Total			.000615	104.6 (2)

VCM-17

Notes:

(1) No estimate or material balance given. Statement made that fugitive emissions are very low due to constant monitoring and good housekeeping.

(2) Based on data provided in June 1974 report. Correspondence with the manufacturer subsequent to the completion of this study indicates total VCM loss may have been as much as ten times higher than value shown.

TABLE VC-3
NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-7
Plant Capacity, Million Lbs./Yr.: 300
Process: Acetylene

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions Lbs./Lb. Prod.	VCM Emissions Tons/Yr.
C	Loading Losses, Max.			.000030	
D	Sampling			.000001	
	Flare Stack		VMD-17	0	
	Fugitive (1)		VMD-3	.000365	
	Total			.000396	59.4

Notes:

(1) This loss estimated by observation as a probable maximum.

TABLE VC-3

NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-8
Plant Capacity, Million Lbs./Yr.: 100
Process: Balanced EDC

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions Lbs./Lb. Prod.	VCM Emissions Tons/Yr.
D	Sampling		VMD-17	.000038	
F	Dryers		VMD-1	.000003	
H_2	Oxychlorination Vent		VMD-1	.001272	
	Waste Heat Boiler Scrubber Vent (1)		VMD-6	.000019	
	Fugitive (2)			.000152	
	Total			.001484	74.2

Notes:

(1) Most of the main vents of the VCM plant are vented to a waste heat boiler along with waste streams from other processes.
(2) By material balance.

TABLE VC-3
NATIONAL EMISSION INVENTORY FOR VCM MANUFACTURE

Plant Code Number: VC-9
Plant Capacity, Million Lbs./Yr.: 275
Process: Acetylene

Source Area	Description	Type Of Emission Control Device	Control Device Catalog I.D. No.	VCM Emissions Lbs./Lb. Prod.	VCM Emissions Tons/Yr.
E	Vent Reactor Vent (1)		VMD-1 & VMD-4(3)	.003561	
	Fugitive (2)			.001515	
	Total			.005076	698.0

Notes:

(1) A secondary reactor is incorporated in this plant to reduce total VCM emissions, but it also has a monetary value in reducing losses significantly.
(2) Estimated from material balance.
(3) No details are given other than the vent are cooled to less than 40°F.

TABLE VC-4
TYPICAL OXYCHLORINATION VENT GAS COMPOSITION (a)
FOR 530 MM LB./YR. ETHYLENE DICHLORIDE PRODUCTION
BY OXYCHLORINATION

(Total EDC Production Required To Produce 700 MM Lb./Yr.
Of VCM By Balanced Ethylene Process)

Component	Normal Range In Composition, Mol.%	Average Flow Rate MPH	Lbs./Hr.
Carbon Dioxide	0.8 - 3.5	36.3	1,598
Carbon Monoxide	0.6 - 1.3	15.7	441
Nitrogen	82 - 95	1,881.5	52,706
Oxygen	0.5 - 7.5	92.6	2,962
Methane	0 - 5.0 (c)	8.1	130
Ethylene	0.2 - 0.8	11.4	318
Ethane	0 - 3.8 (d)	14.5	435
Ethylene Dichloride	0.07 - 0.75	4.6	454
Ethyl Chloride	0 - 0.75	6.0	386
Vinyl Chloride	0 - 0.25	1.6	101 (e)
Aromatic Solvent (b)	0.- 0.1	0.7	71
		2,073.0	59,602

(a) Downstream of water or caustic scrubber facilities. Prior to scrubbing operations, stream normally contains about 65 lbs./hr. HCl.

(b) Only present if aromatic solvent is used for product recovery. (Plant VC-6).

(c) Only present if ethylene and HCl feed to reactors contains methane.

(d) Primarily represents saturate impurity in ethylene feed.

(e) Based on data provided by Plant VC-8, may include some losses from other sources vented through oxychlorination vent stack.

is added downstream of the main oxychlorination reactor in order to convert unreacted ethylene to EDC. By using chlorine for clean-up, it is not essential to obtain maximum conversion in the oxychlorination reactors. This permits a reduction in the amount of excess air employed and also results in a significant reduction in hydrocarbon emissions. According to the survey data, hydrocarbon emissions in the vent gas stream are about half as much as those indicated for plants using several other air oxychlorinated processes. In the plants that have chlorine addition (VC-3, VC-4 and VC-8), the process vent gas is sent to a water or dilute caustic scrubber for removal of HCl (up to 0.0003 T/T VCM) and unreacted chlorine (about 0.0002 T/T VCM) before this stream is emitted to the atmosphere.

In some of the other air oxychlorination plants (VC-6), an absorber-stripper system is used to recover additional chlorinated hydrocarbons from the oxychlorination process vent gas; see Figure VC-2. In these units, a small amount of absorption oil (aromatic solvent) is lost in the atmospheric vent (0.0009 T/T VCM). However, total hydrocarbon emissions are similar to the chlorine addition plants (0.012 T/T VCM).

The oxychlorination vent gas emissions shown in Table VC-4 approximate a weighted average (based on EDC capacity) of emissions from all surveyed air oxychlorination plants. Since about 65% of the air oxychlorination EDC is produced in plants that incorporate absorber-stripper or chlorine recovery systems, the emissions shown in these tables do not truly represent actual values obtained in any specific plant. In other words, units with chlorine addition or lean oil absorption systems would tend to have lower hydrocarbon losses than shown for the "typical unit". Whereas, plants with minimum clean-up facilities would have a somewhat higher level of hydrocarbon emissions.

In the one U.S. oxychlorination plant using tonnage oxygen in place of air (VC-2), total vent gas emissions are greatly reduced. However, hydrocarbon emissions for this unit are similar to those shown in Table VC-4.

5. Direct Chlorination Process Vent - This is the major source of air emissions from the direct chlorination of ethylene. The stream consists of the inerts contained in the reactor effluent (approximately 0.018 lbs./lb. of VCM) plus ethylene (0.0025 lbs./lb. of VCM), ethylene dichloride (0.0016 lbs./lb. of VCM) and small amounts of vinyl chloride.

B. Intermittent Air Emissions

1. Loading Areas - The largest intermittent emissions are from the loading areas. They can be significant if VCM is used for purging oxygen from barges and/or tank cars when this transport equipment is initially placed in service (Source Area C).

2. Storage Vents - Losses from storage of VCM are very low as VCM tanks are pressurized and vents are compressed and recycled (Source Area C).

3. Safety and Relief Valves - This is a small emission and most plants use rupture discs in front of safety valves to minimize leakage.

4. Sampling - This emission is low now because all plants are taking precautions against indiscriminant emissions to protect the Sampler (Source Area D).

5. Filters, Pumps, Etc. - These are mainly fugitive emissions that can vary markedly depending upon condition of equipment. Most companies are monitoring continuously and catch such emissions early (Source Area F).

6. Vessel Openings - Most all equipment is inspected annually and this means opening the equipment. Most companies steam out all vessels and emissions are driven to normal venting areas before vessel is opened (Source Area G).

C. Fugitive Emissions

Fugitive emissions are very low and most are calculated from a material balance. They range from 2 to 50 lbs. per hour. (0.00004 to 0.00150 lbs. VCM/lb. product.)

D. Liquid and Solid Wastes

About 0.0001 T/T VCM of catalyst particles are removed from reject water settling ponds in plants that employ fluidized bed oxychlorination reactors. There are no other solid wastes resulting from VCM production. Liquid wastes are light ends, heavy ends, and water. The light ends are returned to the system for recycle. The heavy ends (liquid chlorinated hydrocarbons) are separated into saleable products, i.e., trichloroethane, trichloroethylene, etc., while the heavier products are generally incinerated. The waste water is generally warmed to allow the VCM vapors to escape to some emission control device (normally a flare or incinerator but sometimes just a high stack).

Table VC-5 and Figure VC-5 show the distribution of reported total VCM emissions in the various VCM plants.

TABLE VC-5

STATISTICAL ANALYSIS OF VCM EMISSIONS

FOR 8 VCM PLANTS IN U.S.

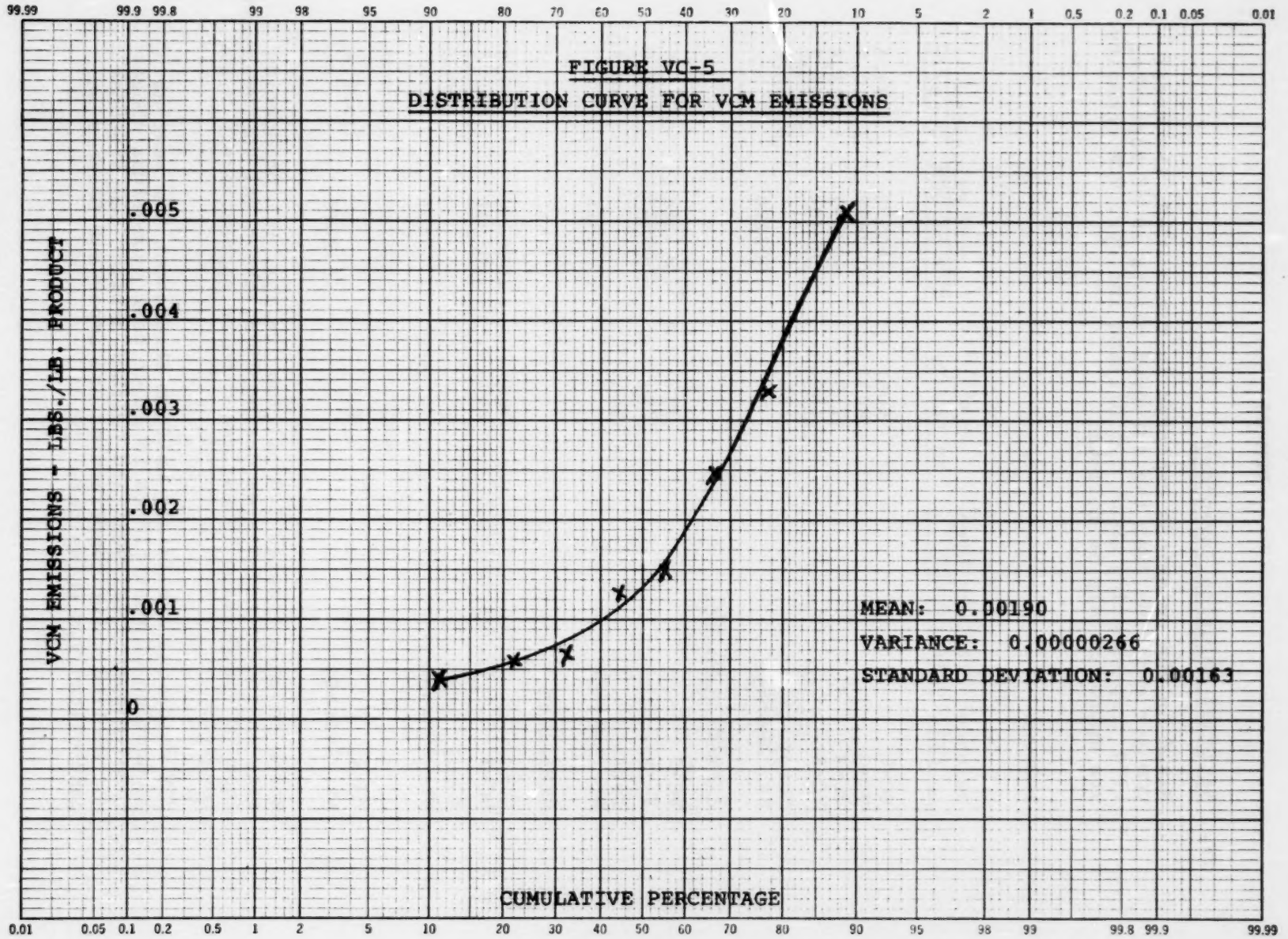
Code No.	Total VCM Emission	Rank No.	Rank No.	Emission	χ^2	Percentile
VC-1	.000578	2	1	.000396	1.56816×10^{-7}	11.1
VC-2	.001264	4	2	.000578	3.34084×10^{-7}	22.2
VC-3	.002478	6	3	.000615	3.78225×10^{-7}	33.3
VC-4	.003297	7	4	.001264	1.597696×10^{-6}	44.4
VC-6	.000615	3	5	.001484	2.202256×10^{-6}	55.6
VC-7	.000396	1	6	.002478	6.140484×10^{-6}	66.7
VC-8	.001484	5	7	.003297	1.08702×10^{-5}	77.8
VC-9	.005076	8	8	.005076	2.576577×10^{-5}	88.9
				.015188	4.7445546×10^{-5}	

Mean = .00190

Variance = .00000266

Standard Deviation = .00163

K+E 18AB X 90 DIVISIONS KEUFFEL & ESSER CO 3000



IV. National Emission Inventory

Based on the emissions reported in Table VC-3, the total VCM air emission from the surveyed plants as of September 1974 (representing about 3.5 billion lbs./yr. VCM capacity) are approximately as follows:

PROCESS

Balanced Ethylene With Pyrolysis of EDC	VCM, MM Lbs/Yr	VCM Emissions T/T of VCM	VCM Emissions Tons/Yr
VC-1	500	.000578	144.5
VC-3	840	.002478	1,040.7
VC-4	730	.003297	1,203.4
VC-8	100	.001484	74.2
Total	2,170		2,462.8
Wt. Average		.002270	
Pyrolysis of EDC			
VC-2	300	.001264	189.6
VC-6	340	.000615	104.6
Total	640		293.2
Wt. Average		.000916	
Acetylene			
VC-7	300	.000396	59.4
VC-9	275	.005076	698.0
Total	575		757.4
Wt. Average		.002634	
Total	3,385		3,513.4
Wt. Average		.002076	

Based on an estimated 5.0 billion lbs./yr. VCM production rate in the United States during 1974, the total VCM emissions from VCM production is estimated to be approximately 5,200 tons/yr.

VCM emissions are fairly uniform throughout the year as production of most plants is at or near (sometimes above) rated capacity all year and neither ambient temperatures nor cooling water temperatures are important factors in controlling VCM emissions.

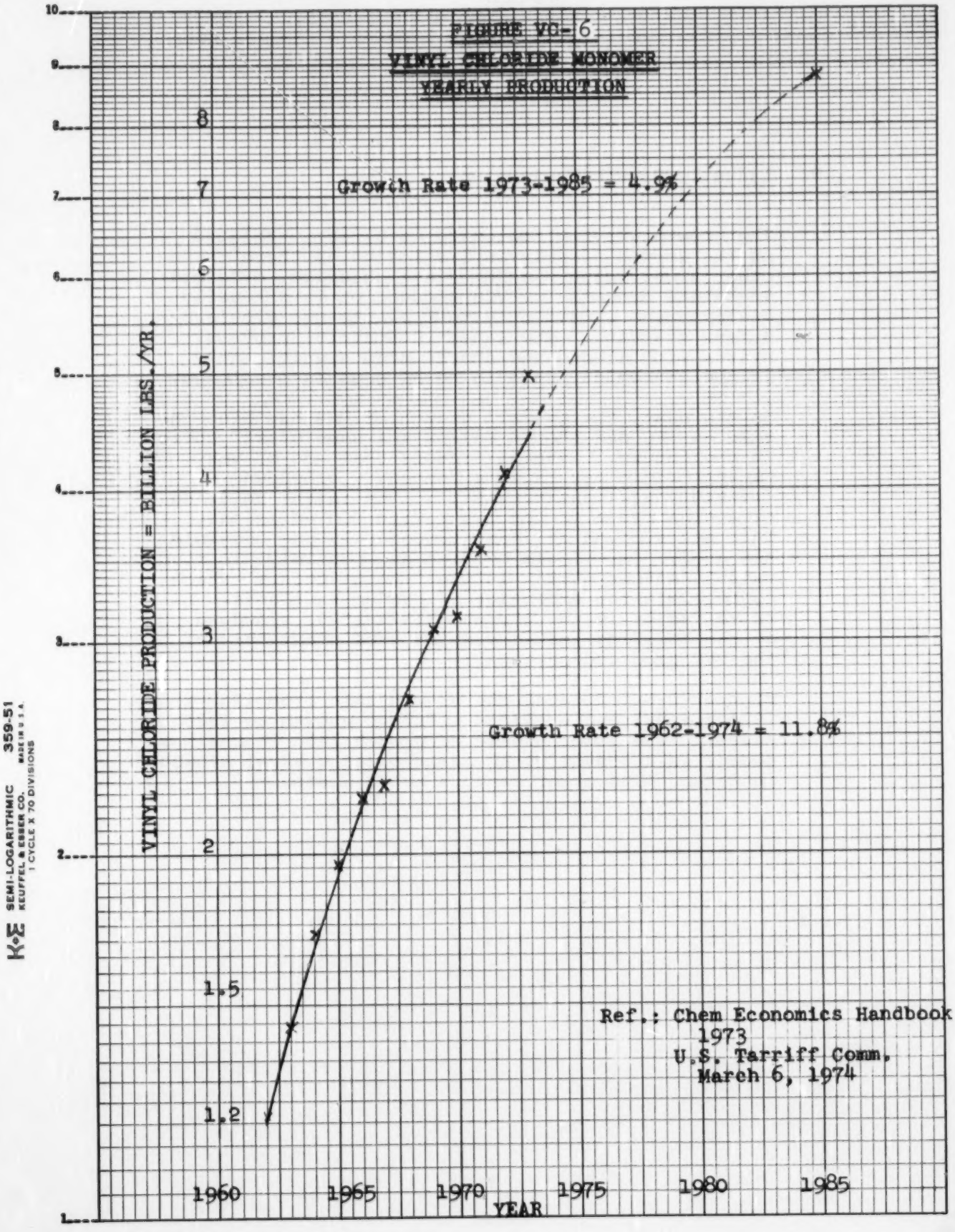
V. Industry Growth Projection

The growth of vinyl chloride is directly related to the growth of polyvinyl chloride as there is no other significant use for vinyl chloride. The old acetylene process for VCM production is gradually disappearing. Currently most plants use dichloroethane cracking. The latest commercial process starts with ethane and should grow significantly if the economics prove to be as good as predicted.

In the past, the overall growth of VCM has been the same as PVC and should follow the same growth curve in the future. Several factors that are of very recent origin may cause a temporary slowdown (possibly a slight reversal). One is the relating of angiosarcoma of the liver with VCM emissions. This has stopped at least temporarily the possible use of PVC for liquor bottles and possibly all food uses. Another factor is the "energy crisis" which could limit the expansion of producing plants. A third factor is the current (1974-1975) slowdown of the building industry which uses about half of the PVC produced nationally.

Figure VC-6 indicates the growth rate from 1962 to 1974 (11.8%) and predicts a future growth to 1985 (4.9%). The lower projected growth rate in the next decade is a result of an anticipated gradual slowdown in demand plus other factors noted above.

FIGURE VC-6
VINYL CHLORIDE MONOMER
YEARLY PRODUCTION



Ref.: Chem Economics Handbook
1973
U.S. Tarriff Comm.
March 6, 1974

K&E SEMI-LOGARITHMIC 359-51
KEUFFEL & ESSER CO. MADE IN U.S.A.
1 CYCLE X 70 DIVISIONS

VI. Emission Control Devices

Any device used to reduce VCM emissions significantly and is not used for any other reasons (i.e., economic) is considered an Emission Control Device. In other words, the device cannot be profitable or it would be a necessary adjunct to the process.

In VCM manufacture, emission control devices rather than control procedures are of primary importance in reducing VCM losses to the atmosphere. This is because VCM manufacture involves a continuous process in which VCM emissions are normally very low (about one-tenth that found in PVC manufacture) and cannot be changed markedly, if at all, by changes in process operating conditions or changes in operating procedural methods. In addition to emission control devices, "good housekeeping" and proper equipment maintenance are important in minimizing VCM emissions.

Listed below are control devices for reducing VCM emissions.

A. Distillation Vents (Source Areas A, A_1, and 7a)

VMD-1 - Stacks

Many of the plants have vent stacks to the atmosphere of varying diameters and heights. Most of the stacks now carrying any significant amount of VCM emissions are to be replaced by a more positive control device. The costs of stacks vary widely depending on height, diameter, location, material, etc.

VMD-2 - Absorbers

The use of EDC as an absorbing media to remove VCM vapors is very effective. After the VCM is recovered from EDC in a stripper, the EDC can be fed back to the pyrolysis unit. In this case, efficient stripping of VCM from the EDC is not essential. Only one company, VC-2, reports using such a system and it is the only plant reporting no continuous emissions other than fugitive emissions. The cost for this system is the cost of piping the vents back to the absorber already in the EDC part of the plant plus any blowers or exhausters necessary to maintain absorber pressure. One plant, VC-6, has plans to use this type system with a calculated 99% VCM recovery efficiency.

VMD-3 - Flares

Three plants, VC-3, VC-6 and VC-7, have vent streams containing VCM along with other combustibles directed to a plant flare. One of these, VC-6, is a pond flare

and the pond is lined with limestone to neutralize the HCl formed at the flare. This flare was installed (1968) at a cost of $16,000 and costs about $25,000/year to maintain with a 20-year life. We have no data on gas composition to the flare.

VC-3 and VC-7 have typical plant flares and the streams contain a substantial amount of VCM and other combustibles. VC-7 contains about 93% combustibles (21% VCM). The flare is 150' high and 6" in diameter. It burns about 280 lbs. VCM per hour (0.0082 lbs./lb. VCM product). No costs are given. VC-3 has a 100 ft. stack (1.17 ft. in diameter). The stream contains about 96% VCM and burns about 345 lbs. of VCM per hour (0.0034 lbs./lb. VCM product). Estimated current cost with necessary piping, knockout pot and refrigeration condenser would be about $200,000. No operating costs were given. Both plants assume that the VCM is completely consumed.

If for any reason these flares go "out" a high emission rate would result.

VMD-4 - Refrigeration

It is possible to reduce VCM emissions by compressing the fractionation vent streams (70 PSIG) and chill the stream (40°F) to condense out most of the VCM and vent the inerts. Such a system for processing the combined distillation vent from a typical 700 MM lbs./yr. plant (see Table VC-1) would cost about $200,000 installed. Assuming the combined feed streams contain 230 lbs./hr. VCM (45 vol.% of stream) about 200 lbs./hr. of VCM (0.0025 lbs./lb. of VCM product) would be recovered. The resulting vent would contain about 0.00038 lbs. of VCM/lb. of VCM product. Electric power consumption for the facility would be 40 KWH/hr. plus 40 GPM cooling water.

VMD-5 - Carbon Adsorption

No plant has mentioned the possibility of using carbon adsorption but it may be a feasible system albeit one requiring considerable development both technically and economically. In a low volume, high percentage VCM content system it would be very effective and fairly economic. In dilute (< 5% VCM) systems it becomes increasingly costly and less feasible technically. Based on processing the combined distillation vent derived from the typical material balance (Table VC-1) we can estimate the size of an appropriate system. Several assumptions must be made as follows:

1) Streams cooled to 85°F to reduce EDC content and improve adsorption.

2) EDC is absorbed by charcoal as easily as VCM.

3) No poisoning contaminants.

The cooled stream would contain approximately 72.5% VCM, 15% EDC and the balance inerts. Under these conditions, using a selected activated carbon[6] of an apparent density of 31 lbs./cu. ft., approximately 1000 cu. ft. of activated carbon would adsorb 99.9+% of the VCM and EDC from the vent streams in a 24-hour on-stream cycle. A second bed of the same size would be required to provide continuous processing. The equipment to handle this adsorption would cost about $200,000 and the double charge of activated carbon (62,000 lbs.) about $80,000.

Utility costs would be high as steam (1000 lbs./hr.) or hot nitrogen (12,000 cu. ft. at 250°-300°F) would be required to regenerate the activated carbon beds. The life of this equipment should be over 15 years and the life of the activated carbon should be 6 to 12 months assuming no positive poisoning ingredient in the vent streams. If there is a poisoning effect or substantial amounts of inerts present, total cost would be much higher.

VMD-6 - Waste Heat Boilers

One company, VC-8, has a waste heat boiler that burns a number of hydrocarbons and chlorocarbons including some VCM. The waste heat boiler is preceded by two parallel caustic scrubbers for removing HCl and Cl_2 from the waste feed gas. The boiler effluent is scrubbed with water to remove HCl before being vented to the atmosphere.

A test was made of this waste heat boiler system by the local Air Pollution Control District. A report was filed in January 2, 1973 giving particulars of the fuel consumption and steam production rates. The stream analytical data presented in this report showed the waste feed gas, during the test, contained less than 1.5% combustibles. One interesting point indicated by the analytical data is that the vinyl chloride was not completely consumed in the combustion chamber but only 98-99% of the VCM was destroyed. Unfortunately, operating temperatures and residence time data were not provided.

An economic analysis of this control device was submitted to the EPA on December 11, 1974 by plant VC-8. According to this economic study, the waste heat boiler operation shows a favorable return on investment. The installed

cost for this facility was $150,000 (in 1972). The waste heat boiler feed consists of 53 CFM of chlorinated waste gases. The heat content of this gas is reported to be 600-1300 BTU/ft.3. This indicates a much higher combustible content than was present during the January 2, 1973 test. Supplemental fuel requirement is 2.1 MM BTU/hr. and the boiler produces 5000 lbs./hr. of steam (average rate). In addition to supplemental fuel, utility costs include $1050/year for electric power and $500/year for water. Cost for chemicals is estimated to be $1000/year. Maintenance charges are estimated at $5,000/year.

Plant VC-1 is installing in 1975, a combination incinerator, waste heat boiler and scrubbers (to remove HCl) at an estimated cost of 2-1/2 million dollars. There is an estimated total annual cost of slightly over 1/2 million dollars but this is offset by an expected heat recovery worth approximately a quarter of a million dollars per year. Only about 20% of this system is directly attributable to VCM plant emission but there is no mention of how much is due to the balanced EDC plant (oxychlorination vent). The incinerator will operate in excess of 1600°F. At this temperature level, they expect the VCM to be completely (100%) destroyed.

B. Oxychlorination Vent Gas (Source Area H_2)

VMD-7 - Thermal Incinerator and Scrubber System

None of the plants covered in this survey presently have an incinerator to burn the oxyhydrochlorination process vent gas. One company (VC-3) has roughly estimated that the capital cost of incinerating the oxyhydrochlorination vent scaled to a 700 MM lbs./year VCM plant would be about $2.5 to 4.25 million dollars with a total annual charge of 0.55 to 0.95 million dollars. In other words, they estimate it would increase the cost of VCM about 1/8 cent per pound to incinerate the vent from the oxychlorination unit. They base their estimate on the experience they are now having with an incinerator designed to handle liquid chlorocarbons. Their proposed system includes an incinerator with support fuel burners, a flue gas quenching system and a flue gas scrubbing system for removal of HCl.

Table VC-6 presents a material balance for thermal incineration and effluent scrubbing of the pseudo typical oxychlorination vent stream (Table VC-4). In order to have essentially complete combustion of pollutants, the incineration is based on an 1800°F combustion zone temperature (0.5 sec. residence time) and 4 mol% (dry basis) oxygen in the effluent. In order to obtain the 1800°F operating temperature, approximately 14 MM BTU/hr. of supplemental fuel is required. Combustion of the oxychlorination vent stream supplies about two-thirds of the required heat. If the actual combustible content of this stream is half of the value assumed, supplemental fuel requirement would be double the value shown.

Since none of the surveyed plants use fired boilers or any other combustion device on this vent stream, it is difficult to predict equipment performance in this application. Based upon applications in other areas, the following potential problems exist:

1) Vent gas is normally available at low pressure.

2) Investment for required blowers, burning equipment and control systems is high.

3) Effluent stream is corrosive at some conditions.

4) Flame control is difficult and flame-outs can be common due to low heating value and low level of incandescence.

5) Operating problem results from need to switch to complete fuel gas firing whenever plant emergency necessitates purging the reactor system with nitrogen. This occurs about twice a year.

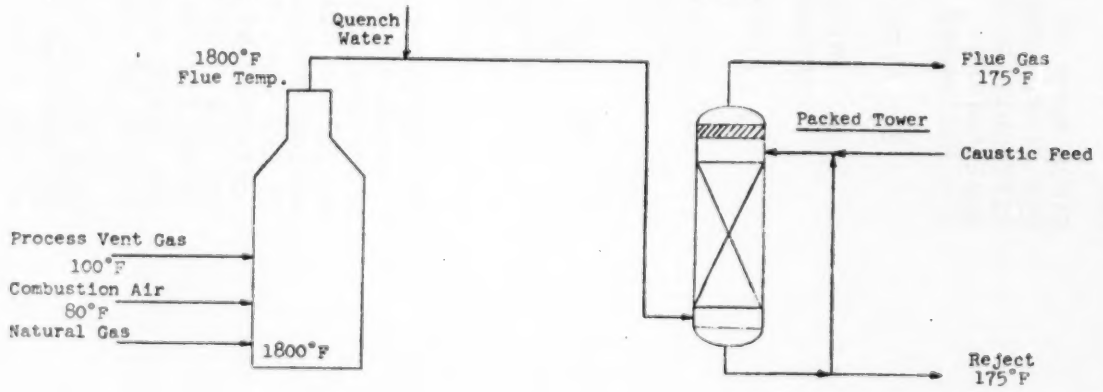
The incinerator effluent is quenched and sent to either a caustic scrubber or combination water-dilute caustic scrubbing unit. The combination unit would be employed if dilute HCl (2-3 wt.% HCl) could be used off-site for stream neutralization or sent to an HCl recovery unit. In the dual scrubbing unit, the gas stream is first contacted with water, which absorbs about 90 percent of the HCl. The gas is then scrubbed with caustic before being discharged to the atmosphere. It is estimated that the stack gases would contain less than one PPM of HCl and 10 PPM by volume of chlorine.

Because of the corrosive properties of the incinerator effluent at low temperature ($<450°F$), the bottom portion of the scrubbing tower and inlet piping would be lined

TABLE VC-6

THERMAL INCINETATOR AND SCRUBBER SYSTEM FOR
530 MM LBS./YR. OXYCHLORINATION PROCESS VENT GAS STREAM

Component	Process Vent Gas	Combustion Air	Natural Gas	Incinerator Flue Gas	Quench Water	Caustic	Scrubber Reject	Scrubber Effluent
Carbon Dioxide	1,598			7,784				7,784
Carbon Monoxide	441							
Nitrogen	52,706	26,752	54	79,512				79,512
Oxygen	2,962	8,126		3,971				3,973
Methane	130		527					
Ethylene	318							
Ethane	435		120					
Ethylene Dichloride	464							
Ethyl Chloride	386							
Vinyl Chloride	101							
Water		460		3,680	56,795		19,034	41,745
Hydrochloric Acid				609				
Chlorine				11				1
Nitrogen Oxides				3				3
Sodium Hydroxide						678		
Sodium Chloride							991	
Total Lbs./Hr.	59,531	35,338	701	95,570	56,795	678	20,025	133,018
SCFM	13,085			21,230				34,690



with fiber reinforced plastics (FRP) or rubber. Porcelain raschig rings, Berl saddles or other types of packing can be used.

Scrubber requirements for processing incinerator effluent from the typical 530 MM lbs./yr. oxychlorination unit are as follows:

	Combination Unit	Caustic Scrubber
Tower Dimensions, Ft.		
Diameter	11	11
T-T Length	35	25
Water Absorption Section		
Number of Beds	2	
Bed Depth, Ft. (each)	8	
Reject Water Rate, GPM	23	
Wash Water Recirculation Rate, GPM	177	
Bed Δ P, Inches of Water	2	
Caustic Scrubbing Section		
Number of Beds	1	2
Bed Depth, Ft. (each)	5	8
Spent Caustic Solution*, GPM	4	40
Caustic Recirculation Rate, GPM	151	155
Bed Δ P, Inches of Water	1	2

* Contains 5.0 weight percent NaCl.

The data presented in Table VC-6 are based on using straight caustic scrubbing without HCl recovery.

Based on published data[4][7] and quotations from incinerator vendors,[8] it is estimated that the approximate cost as of January 1975 for this emission control system would be as follows:

Purchased Cost	
Incinerator	$110,000
Scrubber**	215,000
Total	325,000
Installation Cost	490,000
Total	$815,000

The above total investment for incinerating the oxychlorination vent of a 700 MM lbs./yr. VCM is about one-third the cost projected based on figures provided by plant VC-6. It is difficult to determine installation

** Based on cost data provided by a licenser of oxychlorination process.

charges for installing new equipment in existing plants. In addition the present high rate of inflation makes it difficult to determine equipment costs. However neither of these reasons appear adequate to explain the wide variation in projected capital costs.

In addition to supplemental fuel this emission control device will require 25 KWH/hr. electric power, 115 GPM process water and 650-700 lbs./hr. of caustic.

Most companies considering incinerators, and companies selling this equipment, assume 100% conversion of VCM to HCl, H_2O, and CO_2 is achieved. This assumption may be far from true and performance tests on incineration equipment should be made to determine actual conversion. It is likely that such tests would show a wide variation in VCM combustion efficiency since the operating temperature level and retention time used in the design of this equipment appear to vary markedly.

VMD-8 - Direct Fired Boiler and Scrubber System

A direct fired boiler is another method of oxidizing the oxychlorination process vent.

A large amount of steam is produced in the reactor system of a conventional oxychlorination plant. Even with this production, the overall facility (including direct chlorination and VCM production) usually consumes a substantial quantity of steam (about 2 lbs./lb. of VCM production). Therefore, in new plants, it is conceivable that steam production resulting from pollution control facilities could be used in the VCM complex.

Table VC-7 presents a typical material balance for a fired boiler and scrubber system operating on the clean-up of the oxychlorination vent gas. Incinerator data are based on the same combustion zone operating conditions used for the thermal incinerator. Maximum steam generation is included in order to reduce cost and water requirements for downstream scrubbing facilities.

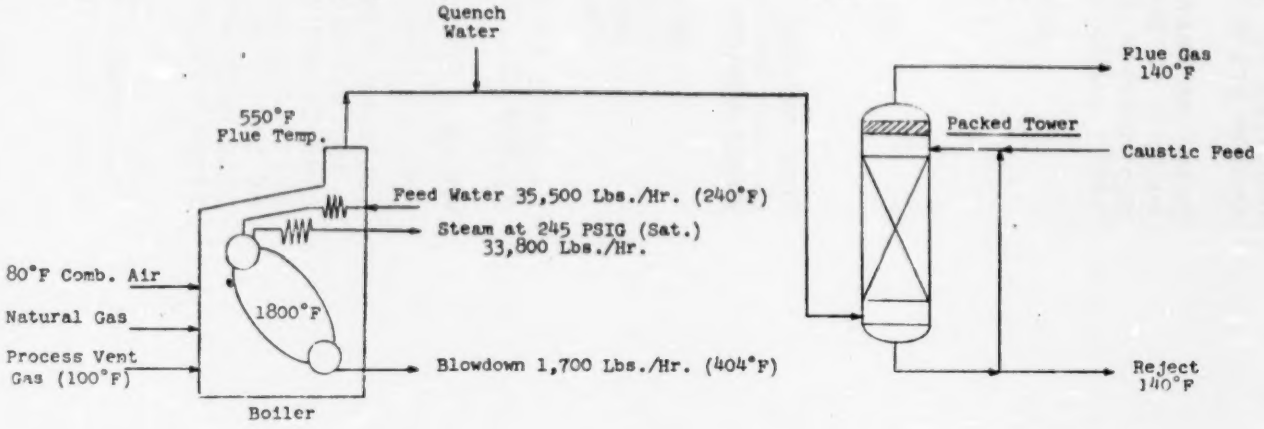
Scrubbing data in Table VC-7 and subsequent economics regarding vent gas incineration effluent scrubbing operations are based on using a caustic scrubber similar to that proposed for the thermal incinerator.

Burning of off-gas in a direct fired boiler results in similar burning problems and combustion efficiency anticipated for a thermal incinerator.

TABLE VC-7

DIRECT FIRED BOILER PLUS SCRUBBER EMISSION CONTROL SYSTEM FOR 530 MM LBS./YR. OXYCHLORINATION PROCESS VENT GAS STREAM

Component	Process Vent Gas	Combustion Air	Natural Gas	Incinerator Flue Gas	Quench Water	Caustic Feed	Scrubber Reject	Scrubber Effluent
Carbon Dioxide	1,598			7,784				7,784
Carbon Monoxide	441							
Nitrogen	52,706	26,752	54	79,511				79,511
Oxygen	2,962	8,126		3,971				3,973
Methane	130		527					
Ethylene	318							
Ethane	435		120					
Ethylene Dichloride	454							
Ethyl Chloride	386							
Vinyl Chloride	101							
Water		460		3,680	27,524		19,034	12,474
Hydrochloric Acid				609				
Chlorine				11				1
Nitrogen Oxides				4				4
Sodium Hydroxide						678		
Sodium Chloride							991	
Total Lbs./Hr.	59,531	35,338	701	95,570	27,524	678	.20,025	103,747
SCFM	13,085			21,230				24,210



In similar applications of fired boilers, it has been found that the effluent stream is especially corrosive at temperatures either above 600°F, or below the HCl dew point. In order to maintain steam coils within the non-corrosive temperature range, 245 PSIG saturated steam is assumed to be generated in the boiler and effluent gases are exhausted at 550°F. Adequate instrumentation is required to see that tube wall temperatures do not exceed 600°F or go below 400°F while burning streams containing chlorinated hydrocarbons. Instrumentation is also required for purging chlorinated compounds from the system prior to furnace shutdown.

Based on data provided in a previous study of air pollution control in EDC manufacture[4], it is estimated that the approximate investment for this control system (January 1975) would be as follows:

Purchased Cost	
Direct Fired	$ 490,000
Scrubber	180,000
Total	$ 670,000
Installation Cost	$1,000,000
Total	$1,670,000

Supplemental fuel requirements are the same as for the thermal incinerator. Estimated utility and chemical requirements are as follows:

Electric Power	-	100 KWH/Hr.
Process Water	-	55 GPM
Boiler Feed Water	-	71 GPM
Caustic	-	650-700 Lbs./Hr.

As noted in Table VC-7, the facility would produce 33,800 lbs./hr. of steam (245 PSIG).

VMD-9 - Incineration Plus Steam Generation and Scrubbing System

Table VC-8 presents a material balance and sketch for a thermal incinerator followed by a waste heat boiler and caustic scrubber. This combination facility has an emissions control efficiency and potential similar to that of the direct fired boiler. The effluent scrubber for this unit would be the same as employed on the direct fired boiler effluent.

There is very little commercial experience of burning chlorinated hydrocarbons in incinerators with steam generation for heat recovery. A Shell Chemical Company

TABLE VC-8

THERMAL INCINERATOR PLUS STEAM GENERATION AND SCRUBBER SYSTEM

FOR

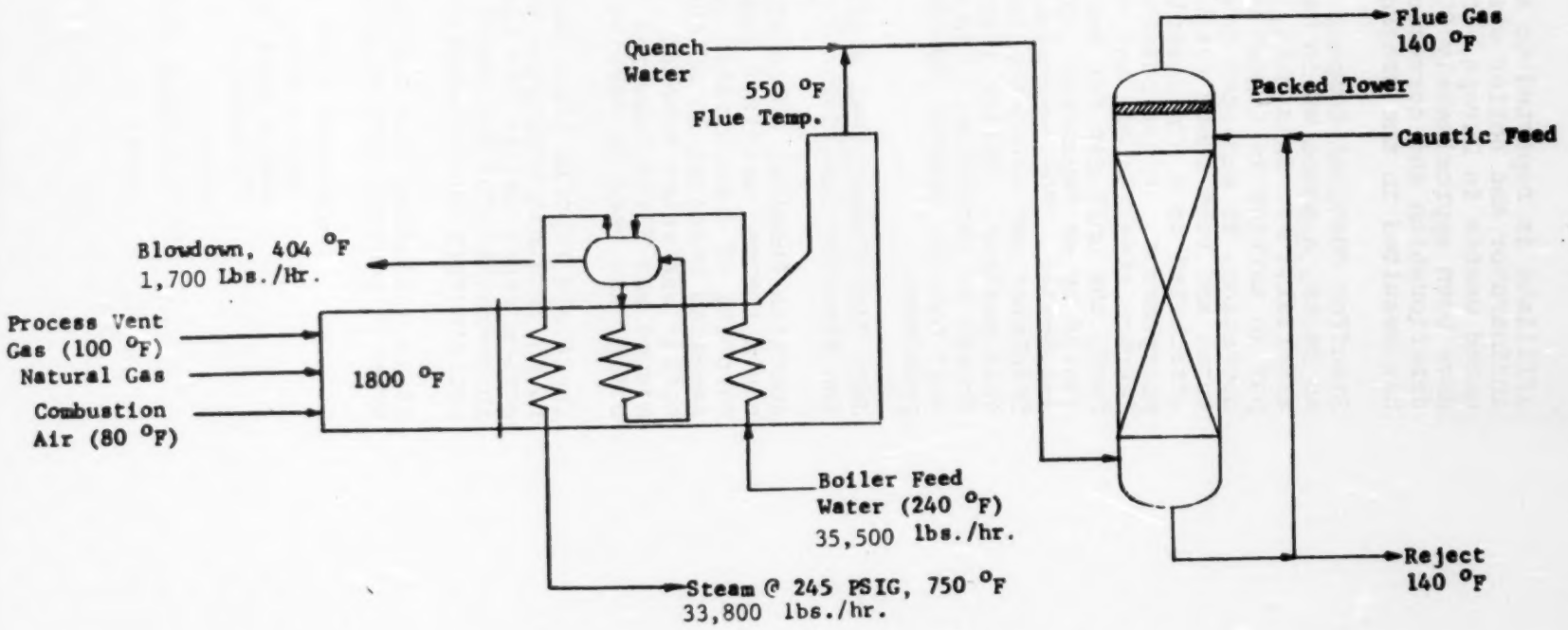
530 MM LB./YR. OXYCHLORINATION PLANT

PROCESS VENT GAS STREAM

MATERIAL BALANCE

Same as shown in Table VC-7

Flow Diagram



affiliate is reported to have had two 100 percent capacity incinerator and boiler systems processing liquid chlorinated wastes in Europe. On-stream factor is believed to have been approximately 25 percent because of brick work deterioration and corrosion problems. This poor performance has resulted in the project being abandoned.

Stauffer Chemical Company has a small fired tube boiler in Bucks, Alabama which burns gaseous chlorinated waste material.(9) This unit, built by John Zink Company, was put in service in August of 1972. After six months operation, it was shut down to replace corroded boiler tubes and tube sheet (carbon steel). Corrosion was attributed to a supplemental feed which contained phosphorous. After retubing one-third of the bundle (carbon steel tubes) and removing phosphorous containing feed, the unit ran for two months before a shutdown was caused by an expansion joint failure between the oxidizer and boiler. The expansion joint had not been packed or insulated and corrosion resulted from condensation during cold weather. Boiler inspection during this shutdown showed no corrosion. Since returning to operation, the unit has run several months with no apparent corrosion problems.

John Zink Company has a pilot unit similar in size to the Stauffer facility.

American Chemical Corporation in Long Beach, California has a thermal oxidizer plus waste heat boiler system for disposal of concentrated gaseous chlorinated hydrocarbons. American Chemical is on its third boiler. The first boiler was water tube and failed within two years. The second was fired tube and lasted five years. The present boiler has been in service two years.

There are reports that there is a B.F. Goodrich licensee, AKZO in Hollandthat employs a thermal incinerator plus a carbon steel boiler for heat recovery. This unit has been in operation for two years and is reported to have given satisfactory performance.

It is estimated that the approximate investment for this type of control system (January 1975) would be as follows:

Purchased Cost	
Incinerator	$ 110,000
Waste Heat Boiler	165,000
Scrubber	180,000
Total	455,000
Installation Cost	685,000
Total	$1,140,000

Utility and chemical requirements for this facility would be the same as for the direct fired boiler system.

VMD-10 - Submerged Thermal Incineration and HCl Recovery

Submerged exhaust incinerators are primarily used in disposal of waste streams that have a high heating value. The main advantage of this incinerator is that effluent gas can be cooled to acceptable scrubber operating temperature and reject a major portion of the HCl as dilute acid (2-5 wt.% HCl) at relatively low capital expense. However, when dealing with low heating value waste streams such as the process vent gas, a substantial amount of supplemental fuel is required to obtain adequate combustion zone temperature (1800°F). While combustion efficiency for this furnace would be similar to other incinerator systems, overall heat utilization is poor and operating costs would be higher than for the above devices with steam generation.

VMD-11 - Catalytic Incinerator

A conventional catalytic incinerator could reduce pollutants to similar levels obtained with a thermal unit. The catalytic facility would operate at lower temperature (800-1000°F) thereby reducing fuel consumption. However, the application of a catalytic incinerator may have the following problems:

1) Only moderate catalyst life with possible danger of catalyst fouling and poisoning.

2) Limited oxidation activity.

3) Based on thermodynamic equilibrium data, low operating temperatures would favor increased chlorine production. Chlorine is more difficult to remove than HCl in downstream scrubbing facilities.

VMD-12 - Flare System

This control device would have the following limitations:

1) A substantial amount of supplemental fuel is required to burn this vent stream. Based on recommendations from vendors, about 125 BTU/SCF is the minimum flareable heating value. This would require about 75 MM BTU/hr. of supplemental fuel.

2) All HCl formed during combustion (about 0.008 lbs./lb. of VCM product) would be emitted to the atmosphere.

3) Efficiency for removing contaminants is less than for other combustion devices. Based upon qualitative data from similar control devices in other applications, it is estimated that approximately 90 percent of the combustibles would be burned.

4) Improper firing of the burner could result in operating temperatures which favor NO_x formation.

5) Changes in vent gas composition could extinguish the burner if adequate instrumentation are not provided.

VMD-13 - Contact Condenser

One plant (VC-5) passes the oxychlorination vent gas through a direct contact condenser to recover EDC (0.015 lbs./lb. VCM product) and other light chlorinated hydrocarbons (0.0015 lbs./lb. VCM). The process vent gas is fed to the tube side of two shell and tube heat exchangers operated in series. In the first exchanger the gas is contacted with an unnamed absorption fluid and indirectly cooled with processed vent gas. In the second exchanger, refrigerant is used to further cool the mixture. Liquid chlorinated hydrocarbons plus absorption fluid are removed from the exchanger effluent in a vapor-liquid separator. A decanting drum is used to separate recovered hydrocarbons from the absorption fluid. The recovered material (90 wt.% EDC) is combined with oxychlorination reactor effluent liquid for water washing and product distillation. The circulating absorption fluid stream is sent to a stripper tower for removal of water. Maloperation of the stripper occasionally results in water recycle and condenser freeze-up.

Since the very limited survey data presented by plant VC-5 did not indicate operating condition and the VCM content of the contact condenser feed and effluent, it is not possible to determine the efficiency of this device for reducing VCM emissions.

VMD-14 - Catalytic Reactor

One plant, VC-4, is installing a catalytic reactor to reduce the total hydrocarbons in the oxychlorination vent. They claim the device will reduce this material by 78%. According to their analysis there is about 0.24% VCM in this stream and about 1.12% of total reactive hydrocarbons (including VCM). The stream contains approximately 4.0% oxidizing materials (oxygen, chlorine and hydrochloric acid). There is no indication as to how

efficient this device is for reducing VCM. There are no conditions given for this reactor nor are any energy requirements noted. A number of catalytic systems are possible but their effectiveness on very dilute streams must be determined experimentally. No economic data were given by plant VC-4 for their catalytic system.

C. Direct Chlorination Process Vent (Source Area H_1)

Most plants employ condensers to recover EDC from this stream before scrubbing the vapor stream and venting the non-condensibles to the atmosphere. Information regarding the VCM content of the vent stream is not available. If VCM is present, this relatively small stream can be sent to the emission control device provided for the oxychlorination process vent.

D. Loading and Storage Vents (Source Area C)

VMD-15 - Refrigeration

Two plants (VC-3 and VC-9) use low temperature refrigeration to recover some VCM and reduce emission to the atmosphere from product storage tanks and loading areas. One, VC-3, maintains -10°F on the outlet vents from these areas. The non-condensibles are sent to a flare. They plan to add another refrigeration unit on the vent from the light ends storage. Each unit represents 10 tons of refrigeration and costs about $100,000 with an annual operating cost of $27,000. The unit for the loading area recovers between 5 to 10 thousand dollars per year of VCM (equivalent to 0.0001 lbs./lb. of VCM product). The new unit on the light ends will recover about $4,000 per year of VCM.

There are no data concerning the refrigeration unit used by VC-9 other than they maintain 35 PSIG pressure on the vent from their vent reactor. The temperature of the vent is kept below 40°F and they recover about 85% of the VCM before the stream is vented to the atmosphere. No cost figures are given by the manufacturer.

VMD-16 - Tank Car And Dock Equalization System

Loading losses of VCM to tank cars or barges is one of the largest sources of VCM emissions at VCM manufacturing plants even though it is an intermittent source. One plant, VC-2, uses an equalization system which equalizes the pressure of the VCM storage tanks with the tank car and barge. Then all VCM vapors from this equalized system are fed back to the EDC absorber and completely recovered.

Actually at the time their report was submitted (Fall of 1974) only the tank car loading facility was equalized but early 1975 they expect the dock facility also to be operative. No cost figures are given, but since the system is primarily piping, the cost is directly dependent upon the distance the loading facilities are from the absorber.

E. Fugitive and Miscellaneous Sources

VMD-17 - Sampling Systems

Most companies are presently taking precautions during sampling that were not considered necessary just over a year ago. Two plants (VC-1 and VC-2) use what they call a continuous loop sampler in which side streams of the main process streams are continuously circulated and can be run through a sampling bomb to purge it completely and then remove the bomb with negligible losses. We have no cost figures for this system but believe it to be under $50,000 for all sampling points. Another plant, VC-3, uses what they call a sealed system. It is somewhat similar to the continuous loop sampler in as much as the sample bomb (cylinder in this case) is purged by the system back to the system but there is no continuous sampling stream. They estimate that it would cost about $25,000 to retrofit their sampling procedure to the continuous system.

VMD-18 - Canned Pumps

There are a considerable number (10-20) high volume VCM pumps required in the average size (700 million lbs./yr.) VCM plant and pump seals are probably the most persistent source of fugitive VCM emissions. The use of canned pumps would eliminate this problem and for a new plant should not increase costs significantly if at all. To replace the VCM pumps now in use at a current VCM plant would cost about $10,000 per pump.

VMD-19 - Monitoring VCM Losses

In order to detect and eliminate leaks as soon as they occur, it is necessary to continuously monitor specific areas for VCM vapors. In a 700 million pounds per year VCM plant probably five ten-point monitors are required to provide adequate coverage. These instruments (chromatographs) cost about $20,000 each. The associated alarm and signal system costs another $30,000, and a data processing system to keep up with the monitors another $40,000 to $90,000. This brings the total cost to about $200,000. In addition, a man is required with a portable VCM detector to follow up alarms as well as monitor

particular areas. He oftentimes will require the assistance of a pipefitter. The monitors (chromatograph) will need fairly continuous servicing by a day time instrument man.

The monitoring of battery limits and off-site VCM concentrations is certainly required initially by most, if not all, plants after allowable limits have been set, but no estimate of this cost is made because of widely divergent conditions for each plant.

VII. Model Plants

To reduce emission of VCM, we have considered two models. In the Model I plant, total VCM emissions other than fugitive would be reduced by about 55-60%. In the Model II plant, the VCM emissions would be reduced about 90%. These percentage reduction figures apply to an average plant.

Listed below are the emission control devices by catalog number for Model Plant I and II and their costs:

Control Device	Device No.	700 MM Lbs/Yr VCM Plant Model I	700 MM Lbs/Yr VCM Plant Model II
Refrigeration	VMD-4	200,000	-
Waste Heat Boiler	VMD-6	-	300,000
Incinerator & Water Heat Boiler	VMD-9	-	1,140,000
Compr. & Refrigeration	VMD-15	200,000	200,000
Cont. Loop Sampler	VMD-17	50,000	50,000
Canned Pumps	VMD-18	-	200,000
Monitoring VCM Leaks	VMD-19	200,000	200,000
		$650,000	$2,090,000

VMD-4 and VMD-15 are refrigeration units to reduce VCM emissions from fractionating columns and loading and storage facilities. Both are definite sources of VCM emissions.

VMD-6 and VMD-9 are waste heat boilers designed to utilize the heating value of the waste gas streams and hopefully to reduce hydrocarbon and chlorocarbon emissions to negligible values (> 98% combustion). They both include scrubbers to reduce resultant hydrogen chloride and chlorine emissions to low values. VMD-6 is used on fairly high chlorocarbon content vent streams from fractionation facilities. The incineration is presumably very efficient (98+%) in reducing VCM emissions. VMD-9 is used to handle the emissions from the oxychlorination unit which has a low VCM and combustible content and is a large volume stream. The efficiency of this incineration is unknown but should be over 98%. The fuel requirement for this waste heat boiler depends on the combustible content of the oxychlorination vent stream. Presumably these two units (VMD-6 and VMD-9) in the Model II plant could be combined into one single waste heat boiler and scrubber at a substantial capital cost savings, say $150,000, if the emission sources were in reasonable proximity.

VMD-17 is a sampling system (primarily piping) so that representative samples can be obtained with minimal material loss and negligible exposure level to sampling personnel.

VMD-18 represents the cost of changing to canned pumps in order to eliminate packing or seal losses which are among the major fugitive VCM losses.

VMD-19 represents the costs of putting in an adequate monitoring system to detect VCM leaks or losses and reduce or eliminate them before they become major emission sources. Most, if not all, VCM plants now have such systems in operation and they have been a major factor in reducing the general level of VCM emissions throughout the industry.

The emission drop to be expected from the various devices for the Model Plants is shown in Table VC-9.

The total emissions shown in Table VC-9 for a typical existing plant without control devices of 0.005435 lbs./lb. product is much higher than the average of 0.001825 shown for all plants in Figure VC-5. This is true for two important reasons, one is that most plants have some emission control devices operating, the other is that most plants have not included emissions from the oxychlorination unit(s) which can be very significant. Model I plant indicates an overall reduction of 55%, allowing for a 25% reduction of fugitive emissions by continuous and careful monitoring. The reduction for the Model II plant is 90%.

The utility requirements of these emission control devices for the Model plants is tabulated below:

Device No.	Model I	Model II
VMD-4		
Electricity	40 KWH/Hr	--
Cooling Water	30 GPM	--
VMD-6		
Electricity	--	45 KWH/Hr
Process Water	--	35 GPM
Boiler Feed Water	--	11 GPM
Caustic	--	650 Lbs/Hr
Fuel	--	2 MM BTU/Hr
Steam Generated (245 PSIG)	--	5,000 Lbs/Hr
VMD-9		
Electricity	--	100 KWH/Hr
Process Water	--	55 GPM
Boiler Feed Water	--	71 GPM
Caustic	--	700 Lbs/Hr
Fuel	--	14-28 MM BTU/Hr
Steam Generated (245 PSIG)	--	33,800 Lbs/Hr
VMD-15		
Electricity	40 KWH/Hr	40 KWH/Hr
Cooling Water	30 GPM	30 GPM
VMD-17 & VMD-19	(No significant utility requirements.)	
VMD-18	(No additional utility requirements over present pumps.)	

TABLE VC-9

VCM EMISSIONS FROM BALANCED ETHYLENE VCM MODEL PLANTS

Typical Existing Plant No Control Devices		Model Plant I			Model Plant II		
Source Area	Lbs/Lb Prod	Cont. Dev. No.	Lbs/Lb Prod	% Eff	Cont. Dev. No.	Lbs/Lb Prod	% Eff
7a	.000500	VMD-4	.000100	80%	VMD-4	.000100	80%
A & A_1	.002400	VMD-4	.000600	75%	VMD-6	.000048	98%
C	.000796	VMD-15	.000119	85%	VMD-15	.000119	85%
D	.000038	VMD-17 (1)	.000009	75%	VMD-17 (1)	.000009	75%
F	.000003	-	.000003	-	-	.000003	-
G	.000078	-	.000078	-	-	.000078	-
H_1 & H_2	.001320	-	.001320	-	VMD-9	.000026	98%
Fugitive	.000300	VMD-19 (2)	.000225	25%	VMD-18 (3) & 19 (2)	.000150	50%
Total	.005435		.002454	55%		.000533	90%

Notes:

(1) One plant reduced sampling losses by 75% using a continuous loop sampler.

(2) Fugitive emissions reduced 25% by careful monitoring and good housekeeping.

(3) Fugitive emissions further reduced by use of canned pumps. The 50% reduction is strictly an assumption, there is no satisfactory data to indicate maximum possible reduction.

Table VC-10 shows the manufacturing costs for a typical existing VCM plant of 700 MM lbs./year productivity without any emission control devices. Table VC-11 shows costs for our Model I and II plants incorporating the emission control devices noted in Table VC-9. Table VC-12 is a Pro Forma Balance sheet for the three plants and indicates the increased capital investment required as more emission devices are employed.

TABLE VC-10

VINYL CHLORIDE MANUFACTURING COST FOR A TYPICAL EXISTING 700 MM LBS./YEAR PLANT

JANUARY 1975

	¢/Lb.	$/Yr.
Direct Manufacturing Cost		
Raw Material		
Ethylene @ 8¢/lb.	3.73	
Chlorine @ 6-1/4¢/lb.	3.67	
Catalyst and Chemicals	0.02	
Labor @ 5 Men/Shift @ $5.65/hr.	0.04	
Maintenance @ 5% of Investment	0.17	
Utilities	0.50	
	8.13	
Indirect Manufacturing Cost		
Plant Overhead (110% Labor)	0.05	
Laboratory (25% Labor)	0.01	
	0.06	
Fixed Manufacturing Cost		
Depreciation (10-yr. Straight Line)	0.35	
Insurance & Property Tax (2.3% Investment)	0.08	
	0.43	
Manufacturing Cost	8.62	
General Expenses		
Administration (3% of Manufacturing Cost)	0.26	
Sales (1% of Manufacturing Cost)	0.09	
Research (2.5% of Manufacturing Cost)	0.21	
Finance (6% of Investment)	0.21	
	0.77	
Total Cost	9.39	65,730,000
Product Value	10.50	73,500,000
Profit Before Taxes	1.11	7,770,000
Profit After 52% Taxes	0.53	3,730,000
ROI (NPAT X 100/Plant Investment)	15.4%	

TABLE VC-11
VINYL CHLORIDE MANUFACTURING COST FOR 700 MM LBS./YR. PLANTS WITH CONTROL DEVICES

JANUARY 1975

	Model I		Model II	
	¢/Lb.	$/Yr.	¢/Lb.	$/Yr.
Direct Manufacturing Cost				
Raw Materials				
Ethylene	3.73		3.73	
Chlorine	3.67		3.67	
Catalyst & Chemicals	0.02		0.14	
Labor @ $5.65/Hr.	0.04	(6 Men/Shift)	0.05	(7 Men/Shift)
Maintenance @ 5% Investment	0.18		0.19	
Utilities	0.50		0.45	
	8.14		8.23	
Indirect Manufacturing Cost				
Plant Overhead (110% Labor)	0.05		0.06	
Laboratory (25% Labor)	0.01		0.01	
	0.06		0.07	
Fixed Manufacturing Cost				
Depreciation (10 yr. st. line)	0.35		0.38	
Insurance & Property Tax (2.3% Investment)	0.08		0.09	
	0.43		0.47	
Manufacturing Cost	8.63		8.77	
General Expenses				
Administration (3% Mfg. Cost)	0.26		0.26	
Sales (1% of Mfg. Cost)	0.09		0.09	
Research (2.5% of Mfg. Cost)	0.21		0.22	
Finance (6% Investment)	0.21		0.23	
	0.77		0.80	
Total Cost	9.40	65,800,000	9.57	66,990,000
Product Value	10.50	73,500,000	10.50	73,500,000
Profit Before Taxes	1.10	7,700,000	0.93	6,510,000
Profit After Taxes	0.53	3,696,000	0.495	3,125,000
ROI (NPAT X 100/Plant Invest.)	14.8%		11.9%	

TABLE VC-12

PRO-FORMA BALANCE SHEET

700 MM LBS./YR. VCM PLANT - BALANCED ETHYLENE PROCESS

JANUARY 1975

Type of Unit	Existing	Improved Existing	
		Model I	Model II
Current Assets			
Cash (1)	$ 5,028,300	$ 5,034,200	$ 5,115,800
Accounts Receivable (2)	6,125,000	6,125,000	6,125,000
Inventories (3)	6,573,000	6,580,000	6,699,000
Fixed Assets			
Plant	23,900,000	24,550,000	25,990,000
Building	250,000	250,000	250,000
Land	100,000	100,000	100,000
Total Assets	$41,976,300	$42,639,200	$44,279,800
Current Liabilities (4)	$ 5,104,200	$ 5,110,000	$ 5,174,200
Equity & Long-Term Dept.	36,872,100	37,529,200	39,105,600
Total Capital	$41,976,300	$42,639,200	$44,279,800

Notes:

(1) Based on one month's total manufacturing cost.
(2) Based on one month's sales.
(3) Based on 10% of annual production at cost.
(4) Based on one month's total cost less fixed manufacturing and finance costs.

VIII. Research and Development Goals

As with PVC plants, the obvious goals are to reduce VCM emissions significantly. However, unlike PVC plants, the emissions from VCM plants are considerably less on a pound per pound basis but considering the large size of most VCM plants, their actual total pounds of emission can be large in a given area.

One of the major sources of VCM emissions is the vent from the oxychlorination unit in the balanced ethylene process. This was not noted in our report on "Ethylene Dichloride by Oxychlorination"[4] At the time of that report, there was no special concern about VCM. Now tests are made to parts per million and it is found that VCM is present in this vent stream, usually several hundred parts per million. The oxychlorination vent stream is a large stream containing small percentage of combustible (<3.0 vol.%). Incinerators, waste heat boilers, etc. are all possible control devices but the first consideration should be to determine how complete the combustion of VCM is under various reasonable conditions of temperature, residence time, and other factors that could effect reaction rates and equilibrium. From data given by plant VC-8, they indicate something under 99% completion and it could be considerably less on very dilute streams.

The possibility of carbon adsorption techniques can only be confirmed by an "in-depth" study of carbon adsorption isotherms on a wide range of chlorocarbons in the presence of water vapor. One of the most important considerations of the many parameters to be studied is the life of the activated charcoal and if there are any "poisoning" ingredients present.

As all the processes involved, direct chlorination (hydrochlorination where acetylene is involved), oxy-chlorination and pyrolysis of EDC are all continuous, there is not much than can be done procedurally to reduce VCM emissions other than close monitoring and good "housekeeping".

One of the two plants using the direct hydrochlorination of acetylene has installed what they term a "vent reactor" on the vent from their main reactor. However, the vent from this "vent reactor" which is cooled to below 40°F (4.4°C) at 35 PSIG emits more VCM than any other single source (on a pound per pound of product basis) of all the VCM plants surveyed. As this process is probably obsolete and the actual production low (far below nameplate capacity),

this particular source of VCM emission may be non-existent in the near future. We would not recommend any research or development program for reducing this emission unless the process should be revived and the plant operated at or near capacity.

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APPENDIX I

BASIS OF THE STUDY

I. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)
Acetic Acid (three processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (two processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (two processes)
Ethylene Oxide (two processes)
Formaldehyde (two processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (two processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (two processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE I
EMISSIONS SUMMARY

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

	ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	125
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY

	Emissions (2), MM Lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM Lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	900	900
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that four additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde, ethylene oxide and high density polyethylene. Consequently, five additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

5. Low pressure catalytic polymerization of Ethylene.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

In addition separate "In-Depth" studies were made on Polyvinyl Chloride (PVC) and Vinyl Chloride Monomer (VCM) using data obtained from a separate survey made in the summer of 1974.